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* NOTICES *

Summary.

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(57) [Abstract]
[Technical problem] It is easy and the electrolytic copper plating method enforced using the electrolytic copper plating equipment using the insoluble anode which can be carried out in high efficiency, and its equipment is offered.
[Means for Solution] In case electrolytic copper plating is carried out in the plating tub containing the galvanized object as cathode used as an insoluble anode and its counter electrode, by the anion exchange membrane, in the copper-ion supply tub classified into the anode plate room which has a metal copper anode plate, and the cathode room containing a sulfuric-acid solution, metal copper is dissolved and a copper ion is supplied into the liquid of an anode plate room. Moreover, the rise of the sulfate-ion concentration in the liquid of the above-mentioned anode plate room is suppressed by connecting the sulfate-ion recovery tub which uses a diffusion-dialysis film, and the above-mentioned cathode room by the circulation relation.

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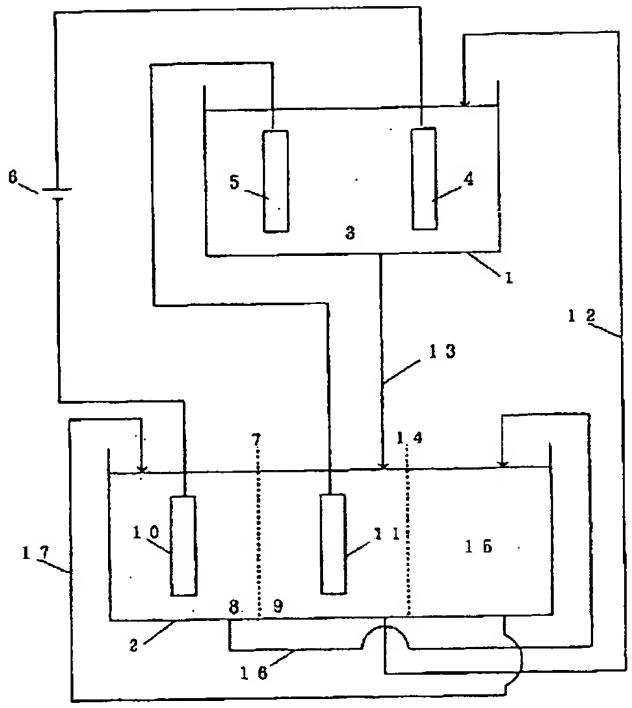

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* NOTICES *

CLAIMS

[Claim(s)]
[Claim 1] (1) Plating liquid which makes a sulfuric acid and a copper sulfate a fundamental component. Plating liquid is contained by the plating tub and (2) anion exchange membranes containing the galvanized object as cathode used as an insoluble anode and its counter electrode, and it is an anode plate. While it is electrolytic copper plating equipment equipped with the above and the aforementioned anode plate room has connected with the aforementioned plating tub by the circulation relation While the anode plate of the aforementioned anode plate room is prepared in the anode plate room of a copper-ion supply tub and the (3) aforementioned copper-ion supply tub which consists of metal copper through a diffusion-dialysis film It is the sulfate-ion recovery tub which contains a

sulfuric-acid solution and collects sulfate ions with a diffusion-dialysis film, and is characterized by containing the sulfate-ion recovery tub connected with the aforementioned cathode room by the circulation relation.

[Claim 2] With equipment according to claim 1, it sets to the (1) aforementioned plating tub in the method of performing electrolytic copper plating. The process which forms a copper-plating coat in the front face of the aforementioned galvanized object by impressing voltage between the aforementioned insoluble anode and the aforementioned cathode, (2) In the process and the (3) aforementioned copper-ion supply tub which supply the plating liquid with which the copper-ion concentration in a process (1) decreased to the aforementioned anode plate room of the aforementioned copper-ion supply tub By electrolyzing between the aforementioned anode plate room and a cathode room, and dissolving the aforementioned metal copper at the aforementioned anode plate room With the process and (4) diffusion-dialysis films which raise the copper-ion concentration of the aforementioned anode plate interior of a room The process which makes a sulfate ion shift to the aforementioned sulfate-ion recovery tub from the aforementioned anode plate room, (5) The process which supplies the plating liquid with which the concentration of a copper ion and a sulfate ion was adjusted to the aforementioned plating tub from the process which supplies the liquid with which sulfate-ion concentration increased to the aforementioned cathode room from the aforementioned sulfate-ion recovery tub, and the (6) aforementioned anode plate room, method characterized by the shell bird clapper.

[Claim 3] (1) Plating liquid which makes a sulfuric acid and a copper sulfate a fundamental component. The anode plate room which contains plating liquid and has an anode plate by the plating tub and (2) anion exchange membranes containing the galvanized object as cathode used as an insoluble anode and its counter electrode. A sulfuric-acid solution is contained and it is cathode. With the copper-ion supply tub which it is electrolytic copper plating equipment equipped with the above, and the anode plate of the aforementioned anode plate room becomes from metal copper, and (3) diffusion-dialysis films The sulfate-ion recovery tub classified into the 2nd tub containing the 1st tub and sulfuric-acid solution containing plating liquid is contained, and the aforementioned plating tub and the aforementioned anode plate room are connected by the circulation relation through the 1st tub of the above, and the aforementioned cathode room and the 2nd tub of the above are characterized by being connected by the circulation relation.

[Claim 4] With equipment according to claim 3, it sets to the (1) aforementioned plating tub in the method of performing electrolytic copper plating. The process which forms a copper-plating coat in the front face of the aforementioned galvanized object by impressing voltage between the aforementioned insoluble anode and the aforementioned cathode, (2) The plating liquid with which the copper-ion concentration in a process (1) decreased is supplied to the 1st tub of the aforementioned sulfate-ion recovery tub. with the aforementioned diffusion-dialysis film By making a sulfate ion shift to the 2nd tub from the 1st tub of the above, to the 1st tub While manufacturing the 1st liquid with which sulfate-ion

concentration fell, to the 2nd tub Electrolyze between the process which manufactures the 2nd liquid with which sulfate-ion concentration increased, the process which supplies the 1st liquid obtained according to (3) processes (2) to an anode plate room, the (4) aforementioned anode plate room, and a cathode room, and the aforementioned metal copper is dissolved at the aforementioned anode plate room. The process which raises the copper-ion concentration of the 1st liquid of the aforementioned anode plate interior of a room, ****** which returns the 1st liquid with which the copper-ion concentration obtained at (5) processes (4) increased to the aforementioned plating tub and the process which circulates through the 2nd liquid obtained according to (6) processes (2) in a cathode room, the method characterized by the shell bird clapper.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] Especially this invention is easy and relates to the electrolytic copper plating method enforced using the electrolytic copper plating equipment using the insoluble anode which can be carried out in high efficiency, and its equipment.
[0002]
[Description of the Prior Art] Usually, when performing electrolytic copper plating, the galvanized object was used for cathode, the soluble anode which turns into an anode plate from metal copper was used, and the copper ion is filled up by the dissolution from this anode plate into the plating liquid with which copper-ion concentration fell. In recent years, technical progress, such as improvement in the speed of plating, has happened, and electrolytic copper plating is becoming the inclination for the distance between electrodes of the anode plate in electroplating and the cathode which is this counter electrode to become shorter from viewpoints, such as improvement in productivity, in connection with this. For this reason, in the aforementioned soluble anode, since the configuration of a plate changes, it cannot respond, and use of an insoluble anode is increasing instead of this. As an insoluble anode, there are a stainless steel electrode, the electrode and carbon electrode which performed platinum plating on titanium, a

ferrite electrode which generally has a form like MO and Fe 2O3 recently.
[0003] When using an insoluble anode, the metaled supply method poses a problem. Conventionally, the metal supply in such a case is used from the point with few copper compounds like a basic copper carbonate than the copper compound of others [influence / on a plating coat], the point with the good solubility over plating liquid, or the point with easy handling. However, the following troubles are mentioned when performing metal supply by the basic copper carbonate.
(1) If the price of a basic copper carbonate is high and makes this the source of supply of a copper ion, increase of plating costs will be caused.
(2) The dissolution in plating liquid takes time, and need the dissolver other than a plating tub.
(3) The impurity contained in the basic copper carbonate may mix into plating liquid, and may do a bad influence to a plating coat.
[0004] Since it is such, the need that other supply methods are considered as the supply method of the copper ion in an electrolytic copper plating bath is increasing. For example, conventionally, an anion exchange membrane is used and the method of performing metal supply is indicated by JP,2-70087,A. Although the solution containing a sulfate ion is put in by this method in order to give electrical conductivity to the cathode room of a metal supply tub, this sulfate ion passes along an anion exchange membrane by the electrodialysis, it moves to an anode plate room, and the sulfate-ion concentration in plating liquid rises gradually. If the sulfate-ion concentration in plating liquid becomes more than anticipated-use concentration, bad influences, such as decline in current efficiency, will begin to arise. Moreover, if a sulfate ion moves to an anode plate room from this cathode room, since anion concentration falls gradually, it will become difficult to hold electrical conductivity in the cathode interior of a room.
[0005]
[Problem(s) to be Solved by the Invention] Therefore, it is easy and this invention aims at offering the electrolytic copper plating method which uses the electrolytic copper plating equipment and it using the insoluble anode which can be carried out in high efficiency.
[0006]
[Means for Solving the Problem] This invention persons are not supply by the basic copper carbonate, as a result of inquiring wholeheartedly, in order to solve the above-mentioned technical problem, they find out that the above-mentioned purpose can be attained by circulating through the plating liquid which held a copper ion and sulfate-ion concentration to fitness by using an anion exchange membrane and a diffusion-dialysis film while supplying with metal copper to a plating tub, and reach this invention. That is, this invention relates to the following invention.
1.(1) By the plating tub and (2) anion exchange membranes containing the plating liquid which makes a sulfuric acid and a copper sulfate a fundamental component, and the galvanized object as cathode used as an insoluble anode and its counter electrode While it is the copper-ion supply tub classified into the cathode room which contains the anode plate room which contains plating liquid

and has an anode plate, and a sulfuric-acid solution, and has cathode and the aforementioned anode plate room has connected with the aforementioned plating tub by the circulation relation While the anode plate of the aforementioned anode plate room is prepared in the anode plate room of a copper-ion supply tub and the (3) aforementioned copper-ion supply tub which consists of metal copper through a diffusion-dialysis film Electrolytic copper plating equipment characterized by containing the sulfate-ion recovery tub which is a sulfate-ion recovery tub which contains a sulfuric-acid solution and collects sulfate ions with a diffusion-dialysis film, and has been connected with the aforementioned cathode room by the circulation relation. 2. In Way Equipment According to Claim 1 Performs Electrolytic Copper Plating (1) in the aforementioned plating tub, by impressing voltage between the aforementioned insoluble anode and the aforementioned cathode In the process and the (3) aforementioned copper-ion supply tub which supply the plating liquid with which the copper-ion concentration in the process and (2) processes (1) which form a copper-plating coat in the front face of the aforementioned galvanized object decreased to the aforementioned anode plate room of the aforementioned copper-ion supply tub By electrolyzing between the aforementioned anode plate room and a cathode room, and dissolving the aforementioned metal copper at the aforementioned anode plate room With the process and (4) diffusion-dialysis films which raise the copper-ion concentration of the aforementioned anode plate interior of a room The process which makes a sulfate ion shift to the aforementioned sulfate-ion recovery tub from the aforementioned anode plate room, (5) The process which supplies the plating liquid with which the concentration of a copper ion and a sulfate ion was adjusted to the aforementioned plating tub from the process which supplies the liquid with which sulfate-ion concentration increased to the aforementioned cathode room from the aforementioned sulfate-ion recovery tub, and the (6) aforementioned anode plate room, method characterized by the shell bird clapper.

3.(1) By the plating tub and (2) anion exchange membranes containing the plating liquid which makes a sulfuric acid and a copper sulfate a fundamental component, and the galvanized object as cathode used as an insoluble anode and its counter electrode With the copper-ion supply tub which it is the copper-ion supply tub classified into the cathode room which contains the anode plate room which contains plating liquid and has an anode plate, and a sulfuric-acid solution, and has cathode, and the anode plate of the aforementioned anode plate room becomes from metal copper, and (3) diffusion-dialysis films The sulfate-ion recovery tub classified into the 2nd tub containing the 1st tub and sulfuric-acid solution containing plating liquid is contained. the aforementioned plating tub and the aforementioned anode plate room It is electrolytic copper plating equipment characterized by being connected by the circulation relation through the 1st tub of the above, and connecting the aforementioned cathode room and the 2nd tub of the above by the circulation relation.

4. In Way Equipment According to Claim 3 Performs Electrolytic Copper Plating (1) in the aforementioned plating tub, by impressing voltage between the aforementioned insoluble anode and the aforementioned cathode The plating

liquid with which the copper-ion concentration in the process and (2) processes (1) which form a copper-plating coat in the front face of the aforementioned galvanized object decreased is supplied to the 1st tub of the aforementioned sulfate-ion recovery tub. with the aforementioned diffusion-dialysis film By making a sulfate ion shift to the 2nd tub from the 1st tub of the above, to the 1st tub While manufacturing the 1st liquid with which sulfate-ion concentration fell, to the 2nd tub Electrolyze between the process which manufactures the 2nd liquid with which sulfate-ion concentration increased, the process which supplies the 1st liquid obtained according to (3) processes (2) to an anode plate room, the (4) aforementioned anode plate room, and a cathode room, and the aforementioned metal copper is dissolved at the aforementioned anode plate room. The process which raises the copper-ion concentration of the 1st liquid of the aforementioned anode plate interior of a room, ****** which returns the 1st liquid with which the copper-ion concentration obtained at (5) processes (4) increased to the aforementioned plating tub and the process which circulates through the 2nd liquid obtained according to (6) processes (2) in the aforementioned cathode room, the method characterized by the shell bird clapper.

[0007] That is, the plating tub equipped with an insoluble anode and the cathode which consists of a galvanized object dissolves copper by preparing the copper-ion supply tub which installed the cathode used as a metal copper anode plate and its counter electrode independently, and impressing voltage to inter-electrode [of a metal copper anode plate and cathode]. However, since copper deposits in the cathode which is a counter electrode with this, a copper-ion supply tub is divided with an anion exchange membrane into an anode plate room and a cathode room, metal copper is used as an anode plate at an anode plate room, and if the cathode used as the counter electrode is installed in a cathode room, the copper ion dissolved by electrolysis will not move to the cathode interior of a room for an anion exchange membrane, but will be accumulated in the anode plate interior of a room. And the plating liquid in a plating tub can be supplied in the form of a metal ion in copper by circulating plating liquid for the anode plate room of a plating tub and this copper-ion supply tub by the pump or other meanses. In this case, although the liquid of the same composition as the plating liquid in the aforementioned plating tub is put into the anode plate room of the aforementioned copper-ion supply tub, in order not to deposit a metal in cathode in the cathode interior of a room and to give electrical conductivity, it is necessary to put in a sulfuric-acid solution.

[0008] However, if it electrolyzes that a copper ion should be supplied in this case, although movement in the cathode room of a cation like a copper ion will not take place by the anion exchange membrane in a metal supply tub, the phenomenon in which the sulfate ion which is an anion moves to an anode plate room by the electrodialysis will occur from a cathode room conversely. Therefore, a means to collect these sulfate ions that went up is needed. This invention persons advanced research further and found out the method of using a diffusion-dialysis film as a method of collecting the sulfate ions condensed in this way. namely, a copper-ion supply tub and one -- or the sulfate-ion recovery tub using a diffusion-dialysis film is prepared as a separate tub for example, the thing

for which a sulfate-ion recovery tub is installed in the anode plate room of a copper-ion supply tub through a diffusion-dialysis film -- the inside of a copper-ion supply tub -- a cathode room -- it classifies into a /anion exchange membrane / anode plate room / diffusion-dialysis film / sulfate-ion recovery tub, and a sulfuric-acid solution is put into a sulfate-ion recovery tub Between a sulfate-ion recovery tub and the anode plate room containing the plating liquid with which sulfate-ion concentration rose, the concentration difference of a sulfate ion arises, this serves as driving force, and movement according [the sulfate ion in plating liquid] to a diffusion dialysis to the sulfate-ion recovery tub from an anode plate room takes place. On the other hand, at a cathode room, when a sulfate ion shifts to an anode plate room, the concentration falls. The liquid with which the sulfate-ion concentration in this cathode room fell is maintainable to the sulfate ion of predetermined concentration by circulating through the liquid with which the sulfate ion was condensed by the sulfate-ion recovery tub with the diffusion-dialysis film.

[0009]

[Embodiments of the Invention] Hereafter, this invention is explained in detail, referring to the drawing about the example of this invention. Drawing 1 is the schematic diagram showing one mode of the desirable electrolytic copper plating equipment of this invention. This electrolytic copper plating equipment consists of compound tubs 2 which combine the plating tub 1, and a copper-ion supply tub and a sulfate-ion recovery tub. The plating liquid 3 which makes a sulfuric acid and a copper sulfate a principal component is contained in the plating tub 1, and while the galvanized object 5 as cathode which turns into an insoluble anode 4 and its counter electrode into plating liquid 3 is arranged, both are electrically connected by DC power supply 6. The compound tub 2 is classified into the 14/sulfate-ion recovery tub 15 of 7/anode plate room 9-/diffusion-dialysis films of cathode room 8-/anion exchange membranes from the anion exchange membrane 7 and the diffusion-dialysis film 14.

[0010] The cathode room 8 contains galvanized objects, such as the body of an automobile, as cathode 10 while containing a sulfuric-acid solution. While the anode plate room 9 contains plating liquid beforehand, the anode plate 11 is formed in it. Moreover, the anode plate room 9 is connected with the plating tub 1 by the circulation relation through piping 12 and 13. The cathode (galvanized object) 10 of the cathode room 8 and the anode plate 11 of the anode plate room 9 are connected through DC power supply 6. The sulfate-ion recovery tub 15 is connected by the circulation relation through piping 16 and 17 in the cathode room 8 while it contains a sulfuric-acid solution. In performing electrolytic copper plating, it sets to the plating tub 1. Voltage is impressed to inter-electrode [of an insoluble anode 4 and the galvanized object 5] by DC power supply 6. by the galvanized object 5 Copper deposits by the reaction of Cu2++2e-->Cu, and oxygen gas occurs in an insoluble anode 4 by the reaction of H2 O+SO42-->1/2(O2) **+SO42-+2e-.

[0011] By the above-mentioned reaction, by the plating tub 1, a copper ion (the 2nd copper ion) is consumed by formation of the plating coat of a galvanized object, and copper-ion concentration falls gradually. Some plating liquid 3 with

which the copper-ion concentration of this plating tub 1 fell is supplied to the anode plate room 9 of the compound tub 2 through piping 13. In the cathode room 8 and the anode plate room 9 of the compound tub 2 Voltage is impressed by DC power supply 6 between cathode 10 and the anode plate 11 which consists of metal copper, and with the metal copper 11 which is an anode plate Cu -> Cu2- + The liquid in which metal copper dissolved into the liquid of the anode plate room 9 as a copper ion, and copper-ion concentration increased by the reaction of 2e- at the anode plate room 9 is obtained. In this case, by the anion exchange membrane 7, since the anion exchange membrane 7 is formed between the cathode room 8 and the anode plate room 9, although a metal does not deposit in cathode 10, while a sulfate ion moves to the anode plate room 9 from the cathode room 8 and the sulfate-ion concentration in the cathode room 8 falls, at the anode plate room 9, sulfate-ion concentration rises at the cathode room 8.

[0012] If sulfate-ion concentration becomes superfluous at the anode plate room 9, the current efficiency of electrolytic copper plating in plating liquid will get worse. Moreover, at the cathode room 8, if sulfate-ion concentration falls, electric conductivity will fall and electrolysis efficiency will fall. For this reason, while reducing the sulfate-ion concentration of the anode plate room 9, a means to increase the sulfate-ion concentration in the cathode room 8 is needed. As this means, by this invention, first, while forming the sulfate-ion recovery tub 15 in the anode plate room 9 through the diffusion-dialysis film 14, the sulfate-ion recovery tub 15 was connected with the cathode room 8 by the circulation relation. That is, since the sulfate-ion recovery tub 15 and the cathode room 8 have a circulation relation through piping 16 and 17, its sulfate-ion concentration is almost the same. If electrolysis advances between the cathode room 8 and the anode plate room 9, a sulfate ion will shift to the anode plate room 9 from the cathode room 8 as mentioned above. Therefore, between the anode plate room 9 and the sulfate-ion recovery tub 15, a difference arises to sulfate-ion concentration. Since the diffusion-dialysis film 14 is formed between the anode plate room 9 and the sulfate-ion recovery tub 15, this concentration difference serves as driving force, and shifts a sulfate ion to the sulfate-ion recovery tub 15 from the anode plate room 9. Consequently, at the anode plate room 9, while sulfate-ion concentration falls, the liquid whose sulfate-ion concentration improved is obtained in the sulfate-ion recovery tub 15. Since the liquid with which the sulfate-ion concentration obtained by the sulfate-ion recovery tub 15 increased is sent to the cathode room 8 which has a circulation relation through piping 17, the sulfate-ion concentration of the liquid in the cathode room 8 returns to the concentration level of a basis again.

[0013] Consequently, since the liquid with which sulfate-ion concentration fell and a copper ion and sulfate-ion concentration were adjusted suitable for the concentration same both almost as plating liquid 3 is obtained at the anode plate room 9 while copper-ion concentration rises By circulating through this liquid to the plating tub 1 through piping 12, the copper ion and sulfate ion of plating liquid 3 in the plating tub 1 can be held by suitable fixed concentration, and electrolytic copper plating can be carried out efficiently. However, the concentration level in

each tub is suitably chosen by the speed of circulation etc. In addition, various kinds of material can be used, without being conventionally, limited especially as an insoluble anode 4 used by this invention, for example, if used as an insoluble anode. As such an insoluble anode, a stainless steel electrode, the electrode and carbon electrode which performed platinum plating on titanium, a ferrite electrode, etc. are mentioned, for example.

[0014] As an anion exchange membrane 7, if a sulfate ion is penetrated, various kinds of anion exchange membranes can be used. As such an anion exchange membrane, the thing of acid resistance, and thermal resistance and organic-proof stain resistance is desirable, for example, Neosepta ACM, Neosepta AMH (tradename of Tokuyama Soda Co., Ltd.), etc. are used suitably, for example. If a sulfate ion is penetrated by diffusion as a diffusion-dialysis film 14 according to a concentration difference, various kinds of diffusion-dialysis films can be used. An anion exchange membrane is also contained in such a diffusion-dialysis film. Specifically as an anion exchange membrane, Neosepta ACM (tradename of Tokuyama Soda Co., Ltd.) etc. can be used, for example. Moreover, as diffusion-dialysis films other than an anion exchange membrane, it is appropriate to, use films, such as Neosepta AFX (tradename of Tokuyama Soda Co., Ltd.), for example.

[0015] Conventionally, even if the organic sulfonic-acid ion under bath increases [in the tin or tin-lead-alloy plating which uses an organic sulfonic acid] by 2 to 5 times the amount of new initial makes-up of electrolytic bath, for example, it is the grade which produces YAKE and there are especially no problem and bird clapper in the high current section. On the other hand, in the electrolytic copper plating by the copper sulfate, when sulfate-ion concentration turns into a 1.5 - double-precision grade of the amount of new initial makes-up of electrolytic bath under bath, the solubility of a copper sulfate falls and there is a problem which the crystal of a copper sulfate forms. For this reason, it becomes indispensable to maintain the sulfate-ion density range under bath in the narrow range strictly by electrolytic copper plating with a copper sulfate. As a suitable method for maintaining sulfate-ion concentration in such a narrow range, it is desirable to enlarge specific surface area of a diffusion-dialysis film. For example, as a specific surface area of a diffusion-dialysis film, they are 10-1000cm2/g and desirable 50-300cm2/g, for example. It is appropriate to use a thing. if it says by the transmission rate of a sulfate ion -- 0.1 - 10 g/hr-dm2 -- 0.5 - 5 g/hr-dm2 is preferably suitable

[0016] In this invention, various kinds of meanses can be used as the circulation means of the plating liquid 3 in piping 12 and 13, and a circulation means of the sulfuric acid by piping 16 and 17. For example, overflow, a pump, etc. can be used. Furthermore, although the DC power supply used by the plating tub 1 and the copper-ion supply tub (it consists of a cathode room 8 and an anode plate room 9) are connected in series, the equipment of this invention may not be limited to such an array, and they may be connected with the separate power supply, respectively. Drawing 2 indicates the electrolytic copper plating equipment of another mode to be electrolytic copper plating equipment of drawing 1 . The electrolytic copper plating equipment of this mode installs the

sulfate-ion recovery tub 19 which consists of the 1st tub 15 and the 2nd tub 20 which were separated with the diffusion-dialysis film 14 as a tub with the copper-ion supply tub 18 separate instead of which consists of a cathode room 8 and an anode plate room 9. [the compound tub 2 in drawing 1]

[0017] It is first put into the liquid of the same composition as plating liquid 1 by this 1st tub 15, and is put into the sulfuric-acid solution by the 2nd tub 20. Moreover, through piping 21 and 22, the 1st tub 15 did as the anode plate room 9 of the plating tub 1 and the copper-ion supply tub 18, and has connected both. On the other hand, the 2nd tub 20 is connected with the copper-ion supply tub 18 by the circulation relation through piping 16 and 17. Like the case of drawing 1 , it is consumed by the electrolytic copper plating in the plating tub 1, and the plating liquid 3 with which copper-ion concentration fell is supplied to the 1st tub 15 of the sulfate-ion recovery tub 19 through piping 21. By the sulfate-ion recovery tub 19, since the diffusion-dialysis film 14 is formed between the 1st tub 15 and the 2nd tub 20, according to a sulfate-ion concentration difference, a sulfate ion moves toward the 2nd tub 20 from the 1st tub 15, the 1st liquid with which sulfate-ion concentration fell forms, and, on the other hand, the 2nd liquid with which sulfate-ion concentration increased forms by the 2nd tub 20 at the 1st tub 15.

[0018] The 1st liquid of the 1st tub 15 is sent to the anode plate room 9 of the copper-ion supply tub 18 through piping 22. In the copper-ion supply tub 18, between the cathode room 8 and the anode plate room 9, voltage is impressed by DC power supply 6 and electrolysis arises. By this electrolysis, a copper ion dissolves from a metal copper anode plate, and copper-ion concentration increases with the 1st liquid of the anode plate room 9. There is almost no influence of the sulfate ion which enters from the cathode room 8 by operation of the anion exchange membrane 7 prepared between the cathode room 8 and the anode plate room 9 at this time since the sulfate-ion concentration in the 1st liquid included in the anode plate room 9 is falling, although a sulfate ion moves toward the anode plate room 9 from the cathode room 8 substantially. On the other hand, since the 2nd tub and the cathode room 8 are connected by the circulation relation, when a sulfate ion moves the sulfate-ion concentration of the 2nd liquid of the cathode room 8 to the anode plate room 9 from the cathode room 8, even if it falls, the sulfate-ion concentration in the cathode room 8 is kept constant by supplying the 2nd liquid from the 2nd tub to the cathode room 8.

[0019] Thus, also in the electrolytic copper plating equipment of drawing 2 , the copper ion and sulfate ion of plating liquid are appropriately held by predetermined concentration.

[0020]

[Example] Below, it explains still in detail, referring to an example about this invention.

Electrolytic copper plating was performed on condition that the following using the equipment of example 1 drawing 1 .

(1) Copper-plating liquid composition A copper ion (it adds as a copper sulfate) 75 g/L A sulfuric acid 190 g/L A chloride ion (it adds as a hydrochloric acid) 50 mg/L (an additive contains the surfactant of a polyoxy-ethylene-glycol system.)

Additive ** Amount
(2) Copper-plating condition current [-- Insoluble anode cathode which gave platinum on titanium / -- Copper plate (3) metal copper anodic-dissolution condition current / -- 10A anode current density / -- 2 A/dm2 anode plate / -- Metal copper anode plate cathode / -- Stainless steel plate (SUS316)] -- 10A cathode current density -- 10 A/dm2 anode plate
(4) In the circulation velocity piping 12 2 In L / distribution tube 13 2 In L / distribution tube 16 2 In L / distribution tube 17 2 The copper-plating liquid of the aforementioned composition is contained in the anode plate room 9 of the plating tub 1 of L / part drawing 1 , and the compound tub 2, and it circulates by piping 12 and 13. Moreover, the sulfuric acid of 150 g/L is contained in the cathode room 8 of the compound tub 2, and the sulfate-ion recovery tub 15, and it circulates by piping 16 and 17. All solution temperature presupposed that it is fixed 30 degrees C, and electrolysis time was performed in 5 hours.
[0021] As an anion exchange membrane 7, Neosepta AMH (the tradename of Tokuyama Soda Co., Ltd., effective-area 4dm2) (specific surface area : 100cm2/g, transmission-rate:1.0 g/hr-dm2 of a sulfate ion) was used, and Neosepta AFX (the tradename of Tokuyama Soda Co., Ltd., effective-area 5dm2) which is an anion exchange membrane was used as a diffusion-dialysis film. The stainless steel plate (SUS316) was used as cathode 10 of the compound tub 2. Change of composition of the plating liquid of this example 1 was shown in the 1st table.
[0022]
[Table 1]
Composition of plating liquid (g/L) <U> Initial composition After [electrolysis] composition Copper ion 75 75 Sulfate ion 190 190 Electrolytic copper plating was performed by the following composition using an example 2, next the equipment of drawing 2 .
(1) Copper-plating liquid composition A copper ion (it adds as a copper sulfate) 75 g/L A sulfuric acid 190 g/L A chloride ion (it adds as a hydrochloric acid) 50 mg/L (an additive contains the surfactant of a polyoxy-ethylene-glycol system.) Additive ** Amount
(2) Copper-plating condition current [-- Insoluble anode cathode which gave platinum on titanium / -- Copper plate (3) metal copper anodic-dissolution condition current / -- 10A anode current density / -- 2 A/dm2 anode plate / -- Metal copper anode plate cathode / -- Stainless steel plate (SUS316)] -- 10A cathode current density -- 10 A/dm2 anode plate
(4) In the circulation velocity piping 12 2 In L / distribution tube 21 2 In L / distribution tube 22 2 In L / distribution tube 16 2 In L / distribution tube 17 2 To the anode plate room 8 of L / part plating tub 1, and the copper-ion supply tub 18, and the 1st tub 15 of the sulfate-ion recovery tub 19, the copper-plating liquid of the above-mentioned composition circulates by piping 12, 21, and 22. Moreover, to the cathode room 8 of the copper-ion supply tub 18, and the 2nd tub 20 of the sulfate-ion recovery tub 19, the sulfuric-acid solution circulates by piping 16 and 17. As an anode plate 11, they were an example 1 and these conditions except having used the metal copper anode plate.

[0023] Change of composition of the plating liquid of this example 2 was shown in the following table 2.
[0024]
[Table 2]
Composition of plating liquid (g/L) Initial composition After [electrolysis] composition Copper ion 75 75 Sulfate ion 190 190 [0025]
[Effect of the Invention] In this invention, while being able to perform supply of the copper ion which ran short easily and cheaply, without affecting composition of plating liquid etc., management of the whole electrolytic copper plating system becomes easy.

[Translation done.]

* NOTICES *

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] The conceptual diagram of the electrolytic copper plating equipment in which the desirable mode of this invention is shown.
[Drawing 2] The conceptual diagram of the electrolytic copper plating equipment in which another desirable mode of this invention is shown.
[Description of Notations]
1 -- Plating tub 3 -- Plating liquid 4 -- Insoluble anode
5 -- Galvanized object 6 -- DC power supply 7 -- Anion exchange membrane
8 -- Cathode room 9 -- Anode plate room 10 -- Cathode
11 -- Metal copper anode plate 14 -- Diffusion-dialysis film 15 -- The 1st tub
18 -- Copper-ion supply tub 19 -- Sulfate-ion recovery tub
12, 13, 16, 17, 21, 22 -- Piping

[Translation done.]

* NOTICES *

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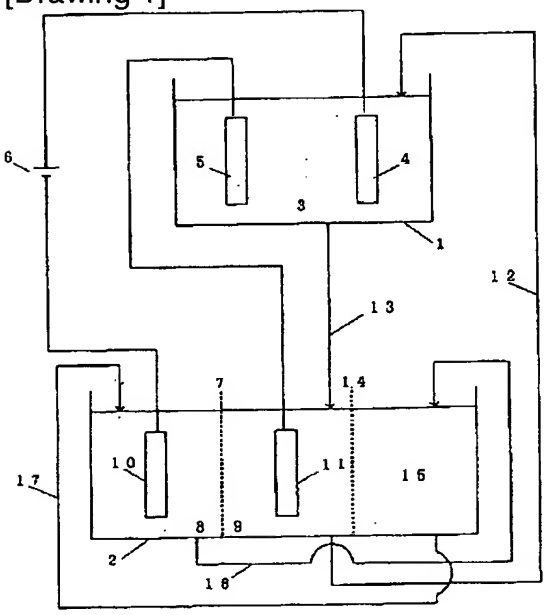
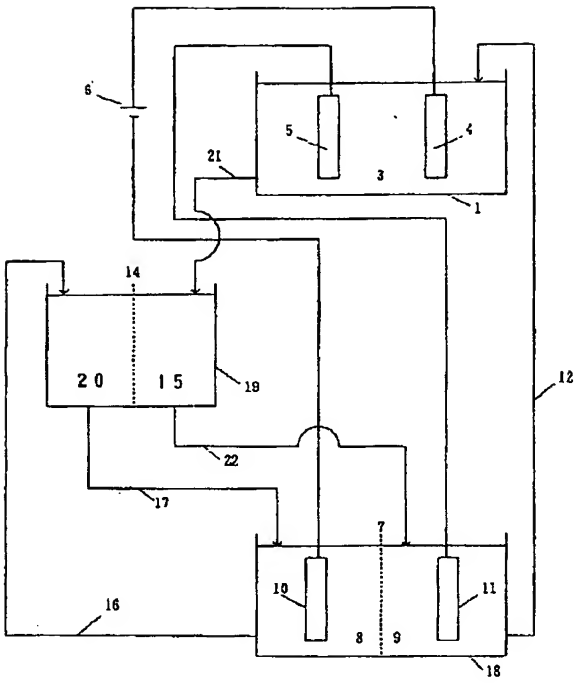
1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DRAWINGS

[Drawing 1]



[Drawing 2]



[Translation done.]